

(19) World Intellectual Property
Organization
International Bureau



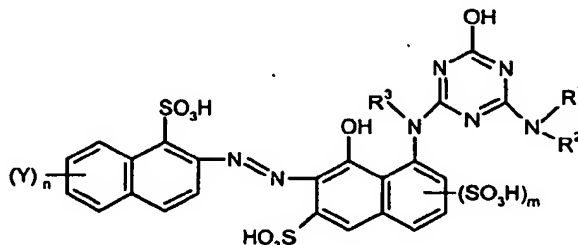
(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/033559 A1

- (51) International Patent Classification⁷: C09B 43/16, C09D 11/02
- (21) International Application Number: PCT/GB2003/004024
- (22) International Filing Date: 19 September 2003 (19.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0223601.6 11 October 2002 (11.10.2002) GB
- (71) Applicant (for all designated States except US): **AVECIA LIMITED** [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SHAWCROSS, Andrew, Paul** [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB). **WIGHT, Paul** [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (74) Agents: **MORPETH, Fraser, Forrest et al.**; Avecia Limited, Intellectual Property Group, P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MONOAZO COMPOUNDS AND INKS CONTAINING THEM



(1)

(57) **Abstract:** A compound of Formula (1) and salts thereof; wherein: R¹ and R³ are each independently H or optionally substituted alkyl; R² is optionally substituted alkyl; Y is OH, CO₂H, SO₃H or PO₃H₂; and n and m each independently have a value of 0 or 1; provided that the compound of Formula (1) is free from fibre reactive groups. Also an ink-jet printing ink, an ink jet printing process, a printed material and an ink jet printer cartridge.

WO 2004/033559 A1

MONOAZO COMPOUNDS AND INKS CONTAINING THEM

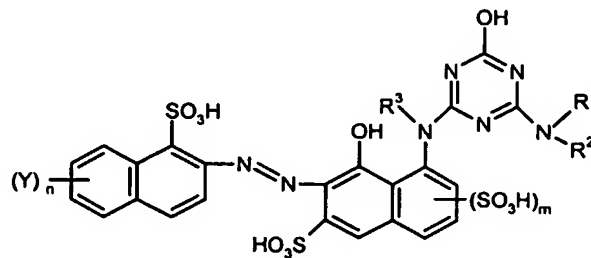
This invention relates to compounds, to inks and to their use in ink-jet printing ("IJP").

IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example, they desirably provide sharp, non-feathered images having good water-fastness, light-fastness, ozone-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle. In particular the developments in IJP technology is leading to more demanding lightfastness performance.

WO99/01510 discloses monoazo dyes carrying a hydroxy triazine group and an aryl amino group.

According to the first aspect of the present invention there is provided a compound of Formula (1) and salts thereof:



Formula (1)

wherein:

R¹ and R³ are each independently H or optionally substituted alkyl;

R² is optionally substituted alkyl;

Y is OH, CO₂H, SO₃H or PO₃H₂; and

n and m each independently have a value of 0 or 1;

provided that the compound of Formula (1) is free from fibre reactive groups.

When the compound of Formula (1) is in the form of a salt it is preferably in the form of a lithium, sodium or potassium salt or a salt with a quaternary ammonium compound, or a mixture thereof. Examples of such salts include NH₄⁺, morpholinium, piperidinium, pyridinium, (CH₃)₃N⁺H, CH₃CH₂CH₂N⁺H₃, CH₃CH₂CH₂N⁺H₃, (CH₃)₂CHN⁺H₃,

$N^+(CH_2CH_3)_4$, N-methyl pyridinium, N,N-dimethyl piperidinium and N,N-dimethyl morpholinium. Especially preferred are ammonium and substituted ammonium salts.

The preferred identity of the optionally substituted alkyl group represented by R^2 and optionally by R^1 depends to some extent on the use to which the compound of Formula (1) will be put.

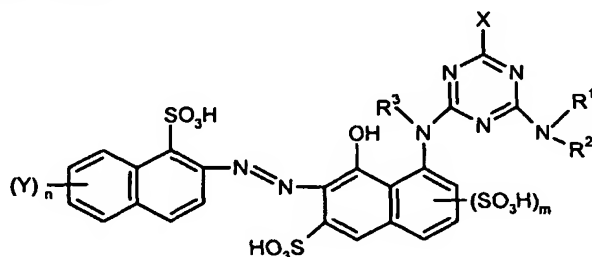
When compounds of Formula (1) are intended for use in aqueous inks the optional substituted alkyl group represented by R^1 and/or R^2 preferably comprises a water-solubilising group. Preferred water-solubilising groups include OH, $-(OCH_2CH_2)_q-$ where q is from 1 to 10, more preferably to 1 to 6, carboxy and sulfo containing moieties and salts thereof. More preferred water solubilising groups are the ionic groups such as carboxy and sulfo containing moieties and the salts thereof. Especially preferred water solubilising ionic groups are carboxylic acid and sulfonic acid groups and salts thereof. Thus for aqueous inks the optionally substituted alkyl group represented by R^1 and/or R^2 is preferably a C_{1-6} -alkyl group carrying a water-solubilising group.

When compounds of Formula (1) are intended for non-aqueous inks the optionally substituted alkyl group represented by R^1 and/or R^2 is preferably hydrophobic. Preferred hydrophobic groups are free from water-solubilising groups. Thus for non-aqueous inks the optionally substituted alkyl group represented by R^1 and/or R^2 is preferably a C_{1-12} -alkyl group free from water-solubilising groups.

The compounds of Formula (1) are free from fibre reactive groups because there is no need for such groups to be present in the compounds and to include them would increase the cost of the compounds. Further such groups tend to hydrolyse and reduce long term ink stability. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of fibre reactive groups excluded from the compounds of Formula (1) there may be mentioned aliphatic sulfonyl groups which contain a sulfate ester group in the beta-position to the sulfur atom, e.g. beta-sulfato-ethylsulfonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids, for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of vinylsulfonyl- or beta-chloroethylsulfonyl- or beta-sulfatoethyl-sulfonyl-endo-methylene cyclohexane carboxylic acids. Other examples of cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl carbonyl; activated halogenated 1,3-dicyanobenzene radicals; and heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms in the heterocyclic

ring and at least one cellulose reactive substituent on a carbon atom of the ring, for example a triazinyl halide. It is preferred that the compounds of Formula (1) are free from fibre reactive groups such as halotriazine, vinyl sulfone and groups convertible to vinyl sulfones on treatment with aqueous alkali, e.g. beta sulfato ethyl sulfone groups.

- 5 The compounds of Formula (1) may be prepared by treatment of a compound of Formula (2) with aqueous base:



Formula (2)

- 10 wherein:

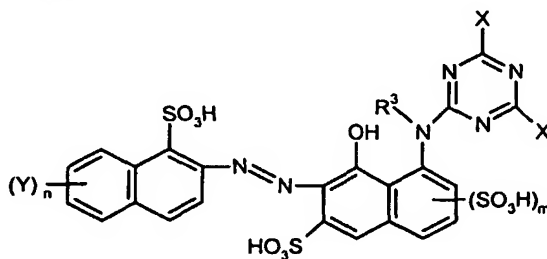
X is a halo; and

R¹, R², R³, Y, m and n are as hereinbefore defined.

The treatment with aqueous base is preferably performed at a temperature of 60 to 100°C, more preferably 70 to 90°C. Treatment times of 2 to 5 hours are typically used.

- 15 Preferred aqueous bases are NaOH, KOH and DABCO.

The compounds of Formula (2) may be prepared by reacting a compound of Formula (3) with an amine of Formula HNR¹R²:



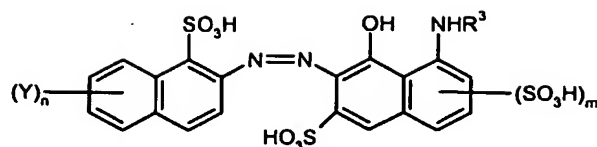
Formula (3)

wherein:

each X independently is halo and Y, n, m and R³ are as hereinbefore defined.

The compounds of Formula (3) may be prepared by condensing a triazine compound carrying three groups represented by X with a compound of Formula (4):

- 25



Formula (4)

wherein Y, n, m and R³ are as hereinbefore defined.

The compounds of Formula (4) may be prepared by diazotising a 1-sulfo-2-amino naphthalene compound carrying n Y groups to give a diazonium compound and coupling the resultant diazonium compound with a 1-hydroxy-8-amino-3-sulfo naphthalene compound optionally carrying a sulfo group at the 5-, 6- or 7-position. Typical diazotisation conditions involve treating the compound with sodium nitrite under acidic conditions at a temperature below 5°C.

The compounds of Formula (1) in salt form may be made from corresponding compounds in the free acid or different salt form using techniques known in the art. For example, an alkali metal salt of a dye may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the dye in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis.

According to a second aspect of the present invention there is provided an ink comprising a compound of Formula (1) or salt thereof and a liquid medium.

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

A preferred ink comprises:

- (a) from 0.01 to 30 parts of a compound of Formula (1) or salt thereof; and
- (b) from 70 to 99.99 parts of a medium comprising component (i), (ii) or (iii):
 - (i) a mixture of water and an organic solvent; or
 - (ii) an organic solvent free from water; or
 - (iii) a low melting point solid;

wherein all parts are by weight and the number of parts (a) + (b) = 100. The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

When the medium is a mixture of water and an organic solvent or an organic solvent free from water, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 70:30.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C₁₈₋₂₄ chains, and sulfonamides. The compound of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

When the dyes according to the present invention exhibit solubility in aqueous media, it is preferred that the liquid medium is a mixture of water and one or more water miscible organic solvent(s).

Preferably the ink according to the second aspect of the present invention is an ink jet printing ink.

The presence of impurities in an ink jet printing ink can result in the formation of precipitates in the ink. This is undesirable because the precipitates can block the narrow ink jet nozzle in the printer. Therefore, the dye(s) according to the present invention are preferably purified to remove undesirable impurities before they are incorporated into inks for ink jet printing. Conventional techniques may be employed for purifying the dyes, for example osmosis and / or dialysis. In particular it is preferable to remove the salts responsible for fouling of the firing head. This fouling is often referred to as kogation and ions such as chloride are particularly undesirable.

Preferably the ink contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions .

Preferably the ink has been filtered through a filter having a mean pore size below 10µm, more preferably below 3µm, especially below 2µm, more especially below 1µm. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

The viscosity of the ink is preferably less than 20 mPa.s, more preferably less than 10 mPa.s, especially less than 5 mPa.s, at 25°C.

The surface tension of the ink is preferably in the range 20-65 dynes/cm, more preferably in the range 30-60 dynes /cm.

The ink may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, pH buffers (e.g. 1:9 citric

acid/sodium citrate) corrosion inhibitors, biocides, kagation reducing additives and surfactants which may be ionic or non-ionic.

According to a third aspect of the present invention there is provided a process for printing an image on a substrate comprising applying an ink according to the second aspect of the present invention to the substrate by means of an ink jet printer.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate used in the third aspect of the invention is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

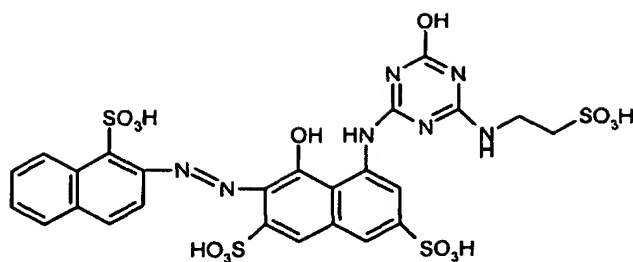
According to a fourth aspect of the present invention there is provided a paper, an overhead projector slide or a textile material printed with an ink according to the second aspect of the present invention, or by means of the process according to the third aspect of the present invention.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

Preferred plastic films are transparent polymeric films, especially those suitable for use as overhead projector slides, for example polyesters (especially polyethylene terephthalate), polycarbonates, polyimides, polystyrenes, polyether sulfones, cellulose diacetate and cellulose triacetate films.

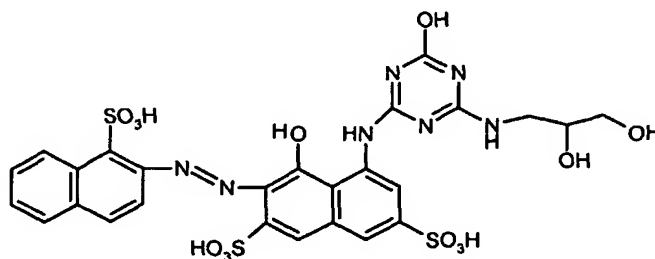
According to a fifth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and an ink wherein the ink is present in the chamber and is as defined in the second aspect of the present invention. The ink jet printer cartridge is optionally refillable.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1Preparation of:

Compound (1)

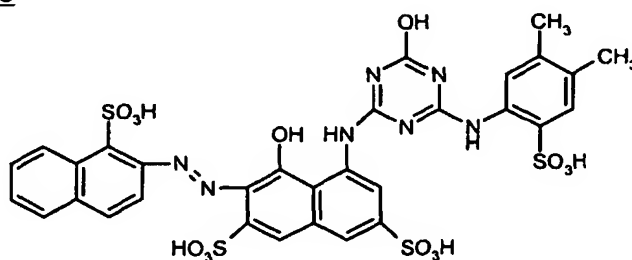
Compound (1) was prepared using the method described in WO 99/01510, Example 1, except that in place of 2-amino benzene sulfonic acid there was used taurine and the resultant dye was not converted to the ammonium salt. The resultant compound had a λ_{max} at 532 nm.

Example 2Preparation of:

Compound (2)

The method of Example 1 was repeated except that in place of taurine there was used 3-Amino-1,2-propanediol.

The resultant Compound (2) had a λ_{max} at 529 nm.

Comparative Example

Comparative Compound

The method of Example 1 was repeated except that in place of taurine there was used 2-amino 4,5 dimethyl benzene sulfonic acid. The resultant Comparative Compound had a λ_{max} at 519nm.

5 Example 3 – Inks & Printing

Ink jet printing inks were prepared having the following formulations:

Ink (1) was prepared by dissolving 2 parts of Compound (1) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone. The pH of the ink was 7.0.

10 Ink (2) and a Comparative Ink were prepared in the same manner as Ink (1) except that Compound (2) and the Comparative Compound were used respectively in place of Compound (1).

Ink Jet Printing

15 The inks were each separately applied to HP Premium Plus paper using a Hewlett Packard HP 660C ink jet printer.

Tests

The following tests were performed on the prints of Ink (2) and the Comparative Ink .

20 The optical density (OD) and CIE colour co-ordinates of each initial print (a, b, L, Chroma "C" and hue "h") were measured using a X-Rite 983™ Spectrodensitometer with 0°/45° measuring geometry, with a spectral range of 400 – 700nm at 20nm spectral intervals, using illuminant C, with a 2° (CIE 1931) observer angle and a density operation status of T. No less than 2 measurements were taken diagonally across a solid colour
25 block on the print with a size greater than 10mm x 10mm.

The prints were exposed to 64 hours in an Atlas Weatherometer.

After the light-fastness tests, the OD and CIE colour co-ordinates were remeasured. The degree of fade ΔE is defined as the overall change in CIE colour co-ordinates L, a, b of the print and is expressed by the equation:

30

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{0.5}$$

The %OD loss is expressed by $\frac{(\text{OD INITIAL} - \text{OD FADE})}{\text{OD INITIAL}} \times 100$

35

Best light fastness corresponds to lowest ΔE and % OD loss values.

	<u>OD INITIAL</u>	<u>% OD LOSS</u>	<u>ΔE</u>
Comparative Ink	1.078	74%	49
Comparative Ink	0.498	72%	34
Ink (2)	1.096	45%	26
Ink (2)	0.558	44%	20

As can be seen, the Compound (2) of the present invention in Ink (2) gives excellent light fastness.

5 Example 4

The inks described in Tables I and II may be prepared wherein the compound described in the first column is the compound made in the above Example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na₂HPO₄ and

TBT = tertiary butanol

TDG = 1,3-bis(2-hydroxyethyl) urea

TABLE I

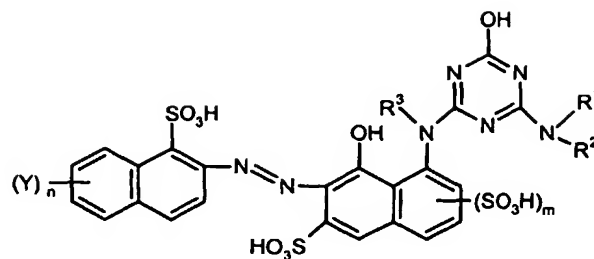
Compound	Compound Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	4.8		0.2					
1	10.0	85	3		3	3				5	1	
2	2.1	91		8								1
1	3.1	86	4.8				0.2	4				5
2	1.1	81			9		0.5				9	
1	2.5	60	4	15	3	3		6			5	4
2	5	65		20				10				
1	2.4	75	5	4		5				6		5
2	4.1	80	3	5	2	9.7	0.3					
1	3.2	65		5	4	6			5	4	6	5
2	5.1	96								4		
1	10.8	90	5						5			
2	10.0	80	2	6	2	5			1		4	
1	1.8	80		5							15	
2	2.6	84			11						5	
1	3.3	80	2			10				2		6
2	12.0	90				6.7	0.3	3				
1	5.4	69	2	20	2	1					3	3
2	6.0	91			4						5	

TABLE II

Compound	Dye Compound	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					4.8	
2	9.0	90		5						1.2		3.8
1	1.5	85	5	5		0.15	4.65	0.2				
2	2.5	90		6	3.88					0.12		
1	3.1	82	4	7.7		0.3						6
2	0.9	85		10					4.8	0.2		
1	8.0	90		5	4.7			0.3				
2	4.0	70		10	4				1		4	11
1	2.2	75	4	10	3				2		6	
2	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	4.05	
2	5.0	78	5	11							6	
1	5.4	86			7						7	
2	2.1	70	5	5	5	0.1	0.2	4.6	5	0.1	5	
1	2.0	90		10								
2	2	88			2			10				
1	5	78			5			12			5	
2	8	70	2		8			15			5	
1	10	80						8			12	
2	10	80		10								

CLAIMS

1. A compound of Formula (1) and salts thereof:



Formula (1)

wherein:

R^1 and R^3 are each independently H or optionally substituted alkyl;

R^2 is optionally substituted alkyl;

Y is OH, CO_2H , SO_3H or PO_3H_2 ; and

n and m each independently have a value of 0 or 1;

provided that the compound of Formula (1) is free from fibre reactive groups.

2. A compound according to claim 1 wherein the compound of Formula (1) is in the form of a lithium, sodium, potassium or quaternary ammonium salt, or a mixture thereof.

3. A compound according to claim 1 or 2 wherein R^1 and/or R^2 comprise a water-solubilising group.

4. A compound according to claim 3 wherein the water-solubilising group is ionic.

5. A compound according to claim 1 or 2 wherein R^1 and/or R^2 is a C_{1-12} -alkyl group free from water-solubilising groups.

6. An ink comprising a compound according to any one of the preceding claims and a liquid medium.

7. An ink comprising:

- (a) from 0.01 to 30 parts of a compound according to any of claims 1 to 5;
and

- (b) from 70 to 99.99 parts of a medium comprising component (i), (ii) of (iii):

- (i) a mixture of water and an organic solvent; or

- (ii) an organic solvent free from water; or
- (iii) a low melting point solid;

wherein all parts are by weight and the number of parts (a) + (b) = 100.

5 8. An ink jet printing ink according to claim 6 or 7.

9. A process for printing an image on a substrate comprising applying an ink according to claim 8 to the substrate by means of an ink jet printer.

10 10. A paper, an overhead projector slide or a textile material printed with an ink according to claim 8 by means of a process according to claim 9.

11. An ink jet printer cartridge containing an ink according to claim 8.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/04024

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B43/16 C09D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 406 527 B1 (PEDRAZZI REINHARD ET AL) 18 June 2002 (2002-06-18) claims; example 12 ---	1-3,5-11
X	EP 0 866 105 A (MITSUBISHI CHEM CORP) 23 September 1998 (1998-09-23) page 24, compound 50; page 7, lines 34-41; claims ---	1-4,6-11
X	EP 1 036 823 A (CLARIANT GMBH) 20 September 2000 (2000-09-20) claims; example 11 ---	1-4,6-11
X	EP 0 559 310 A (ZENECA LTD) 8 September 1993 (1993-09-08) claims; example 12 ---	1-4,6-11
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

17 December 2003

Date of mailing of the international search report

29/12/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ginoux, C

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/GB 03/04024

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 036 (C-328), 13 February 1986 (1986-02-13) -& JP 60 188468 A (NIPPON KAYAKU KK), 25 September 1985 (1985-09-25) abstract; examples 21-23 -----	1-11
Y	WO 99 01510 A (KENWORTHY MARK ;ZENECA LTD (GB)) 14 January 1999 (1999-01-14) cited in the application page 5, line 17 - line 23; examples -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/04024

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6406527	B1	18-06-2002	DE 19911195 A1	14-09-2000
			DE 50000894 D1	23-01-2003
			EP 1036822 A1	20-09-2000
			JP 2000327938 A	28-11-2000
EP 0866105	A	23-09-1998	DE 69803612 D1	14-03-2002
			DE 69803612 T2	08-08-2002
			EP 0866105 A2	23-09-1998
			JP 11158429 A	15-06-1999
			US 5993525 A	30-11-1999
EP 1036823	A	20-09-2000	DE 19911536 A1	21-09-2000
			DE 50003156 D1	11-09-2003
			EP 1036823 A1	20-09-2000
			JP 2000297222 A	24-10-2000
			US 6432185 B1	13-08-2002
EP 0559310	A	08-09-1993	AT 136324 T	15-04-1996
			AU 3102693 A	09-09-1993
			CA 2087489 A1	07-09-1993
			DE 69302039 D1	09-05-1996
			DE 69302039 T2	12-09-1996
			EP 0559310 A1	08-09-1993
			JP 5311087 A	22-11-1993
			US 5383960 A	24-01-1995
JP 60188468	A	25-09-1985	JP 1053976 B	16-11-1989
			JP 1629565 C	20-12-1991
WO 9901510	A	14-01-1999	AU 8121898 A	25-01-1999
			AU 8121998 A	25-01-1999
			CN 1105152 B	09-04-2003
			DE 69807490 D1	02-10-2002
			DE 69808913 D1	28-11-2002
			DE 69808913 T2	18-06-2003
			EP 0994924 A1	26-04-2000
			EP 0994925 A1	26-04-2000
			WO 9901510 A1	14-01-1999
			WO 9901513 A1	14-01-1999
			JP 2002508806 T	19-03-2002
			JP 2002510350 T	02-04-2002
			US 6379442 B1	30-04-2002
			US 6344076 B1	05-02-2002